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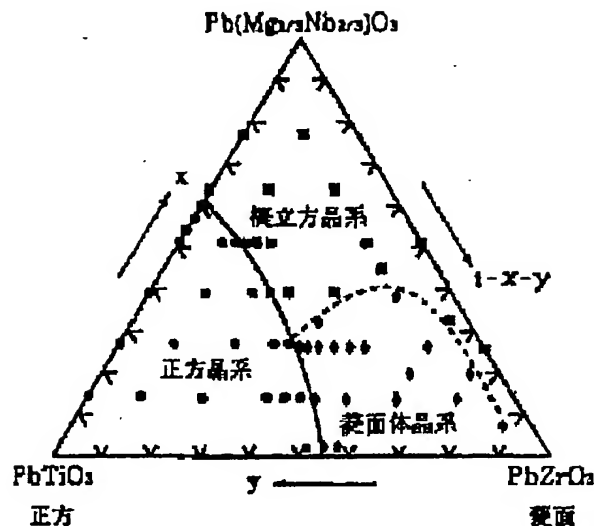
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TITLE : PIEZOELECTRIC MATERIAL AND ITS
PRODUCTION AND PIEZOELECTRIC
OSCILLATOR AND PIEZOELECTRIC
SOUNDING BODY USING THE SAME



ABSTRACT : PROBLEM TO BE SOLVED: To stably obtain a piezoelectric material comprising a material composition having a composition of phase boundary between a good tetragonal system and a good rhombohedral system, in an oxide ferroelectric ceramic used for various kinds of electronic parts, and to use a particle diameter-controlling agent capable of sufficiently pulling out the performances of the piezoelectric material and simultaneously controlling the sizes of grains, in a piezoelectric sounding body requiring a highly strong and compact ceramic.

SOLUTION: This piezoelectric material containing as a main component a perovskite type oxide containing iron is produced by calcining a material of the formula $(\text{Pb}_{1-x-\alpha}\text{M}_\alpha)(\text{Zr}_{1-y}\text{Ti}_y)_{1-z}(\text{Mg}_{2/3}\text{Nb}_{1/3})_z\text{O}_3$ [M is at least one element selected from Ba, Bi and Sr; $0 \leq (\alpha) < 0.10$; $0.20 < (y) < 0.30$; $0.45 < (z) < 0.55$, adding MgNb_2O_6 of columbite type oxide as a grain diameter-controlling agent in an amount range: $0.005 < (x) < 0.05$ based on Pb and again calcining the mixture.

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(54) 【発明の名称】 圧電材料およびその製造方法およびそれを用いた圧電振動子および圧電発音体

(57) 【要約】

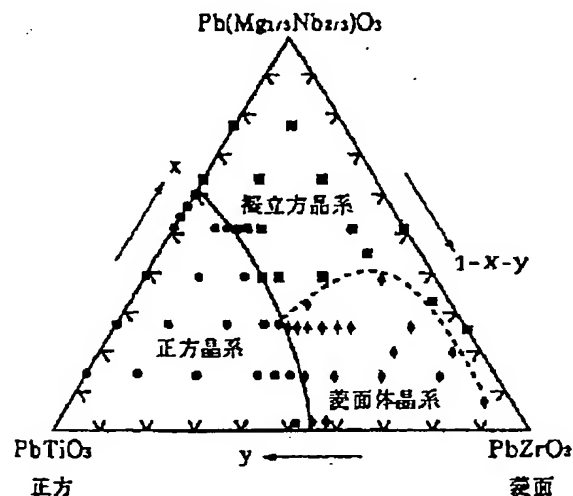
【課題】 各種電子部品に使用される酸化物強誘電体のセラミクスにおいて、圧電材料が良好な正方晶系と菱面体晶系の相境界の組成物の材料組成で良好な圧電特性を有しかつ耐熱性の高い圧電材料を安定に得ること。また、高強度で緻密なセラミックが要求される圧電発音体において、圧電材料の性能を十分に引き出しながらグレインサイズの制御が可能な粒径制御剤を使用すること。

【解決手段】 鉛を含むペロブスカイト型酸化物を主成分とする圧電材料において、

【数1】

$$(\text{Pb}_{1-x-y}\text{M}_x)(\text{Zr}_{1-y}\text{Ti}_y)_{1-z}(\text{Mg}_{1/3}\text{Nb}_{2/3})_z\text{O}_3$$

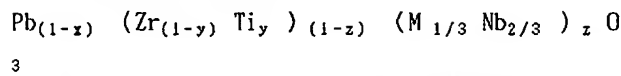
(MはBa、Bi、Srから選ばれる少なくとも1種の元素、 $0 \leq x < 0.10$) なる化学式で表わされ、 $0.20 < y < 0.30$ 、 $0.45 < z < 0.55$ の範囲で材料を仮焼成後、粒径制御剤としてコランバイト型酸化物である MgNb_2O_6 をPbに対して $0.005 < x < 0.05$ の範囲で添加し再び仮焼成を行う。



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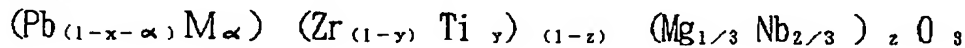
【特許請求の範囲】

【請求項1】 鉛を含むペロブスカイト型酸化物を主成分とする圧電材料において、



(Mは、Mg、Ni、Znのうちから選択される少なくとも1種類の元素)

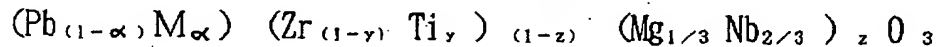
なる化学式で表わされ、かつ $0.005 < x < 0.05$



(Mは、Ba、Bi、Srのうちから選択される少なくとも1種類の元素、 $0 \leq \alpha < 0.10$)

なる化学式で表わされ、かつ $0.005 < x < 0.05$ 、

$0.20 < y < 0.30$ 、 $0.45 < z < 0.55$ の範囲にあるように組成を設定したことを特徴とする圧電材料。



(Mは、Ba、Bi、Srのうちから選択される少なくとも1種類の元素、 $0 \leq \alpha < 0.10$)

なる化学式で表わされ、かつ $0.20 < y < 0.30$ 、 $0.45 < z < 0.55$ の範囲にあるように材料を仮焼成後、粒径制御材としてコランバイト型酸化物である MgNb_2O_6 をPbに対して $0.005 < x < 0.05$ の範囲にあるように添加し、再び仮焼成を行う圧電材料の製造方法。

【請求項6】 請求項5記載の圧電材料の製造方法で得られるグレインサイズが $5\mu\text{m}$ 以下である圧電材料。

【請求項7】 請求項1から4のいずれか、または請求項6に記載の圧電材料を用いたことを特徴とする圧電振動子。

【請求項8】 厚みが $50\mu\text{m}$ 以下の請求項7に記載の圧電材料を用いた圧電振動子。

【請求項9】 請求項7または8記載の圧電振動子を用いたことを特徴とする圧電発音体。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、携帯電話、コンピュータ等の発音源に用いられる圧電材料およびその製造方法およびそれを用いた圧電振動子および圧電発音体に関する。

【0002】

【従来の技術】近年、圧電材料を用いた圧電スピーカやレシーバは、携帯電話やコンピュータの音声出力装置として見直されてきている。特に携帯用として摂氏 200°C 以上の高温で安定に動作する圧電振動子への要望が強くなっている。このとき問題となるのが、1) 耐熱性、2) 圧電特性、3) 信頼性、といったことである。そのため、ペロブスカイト構造を有する酸化物強誘電体のセラミクスに着眼した新材料の探索と添加物による改善が

5、 $0.50 < y < 0.80$ 、 $0.35 < z < 0.65$ の範囲にあるように組成を設定したことを特徴とする圧電材料。

【請求項2】 摂氏 200°C 以上のキュリー点を有することを特徴とする請求項1記載の圧電材料。

【請求項3】 鉛を含むペロブスカイト型酸化物を主成分とする圧電材料において、

【数1】

【請求項4】 グレインサイズが $5\mu\text{m}$ 以下であることを特徴とする請求項1から3のいずれかに記載の圧電材料。

【請求項5】 鉛を含むペロブスカイト型酸化物を主成分とする圧電材料において、

【数2】

多数行われている。

【0003】酸化物強誘電体のセラミクスにおいて圧電特性を向上しようとする、キュリー点(強誘電相と常誘電相の転移温度)が下がってしまい、耐熱性が悪くなってしまう。要望される良好な特性を得るためには、耐熱性をある程度ゆずってキュリー点を 200°C 未満とし、材料を使用する際に、耐熱性に注意を払う必要があった。この結果、材料からの取り出し電極の電気接続工程において、特性が変化してしまうという問題があった。

【0004】また、デバイス設計から要望されているキュリー点が摂氏 200°C 以上となる組成では、大きな圧電特性が得られなくなり、圧電特性に対する要望に応えられなくなってしまうという問題があった。

【0005】

【発明が解決しようとする課題】そこで、所望される良好な特性を得るための材料探索として、第3の組成物となる複合ペロブスカイト型酸化物をさらに混合したり、新たに添加物を加えることが多く研究されてきているが、第3の組成物を混合することによってペロブスカイト構造以外の誘電率の低い別の結晶構造を持つ化合物が二次的に形成され、本来の圧電特性が得られなくなってしまうという新たな課題が発生した。

【0006】また、デバイスは、より小型化・薄型化を要望されており、そのために薄膜のセラミックスの要望が高まってきている。圧電発音体として 2mm 以下の発音体の要望がでてきているが、これに応えようとする、発音体の設計上セラミック素子として $50\mu\text{m}$ 以下の薄膜のセラミックが必要となってきた。

【0007】さらに、圧電発音体に用いられるセラミックは、積層セラミックコンデンサやアクチュエータのような積層タイプと違い、単層で金属板に張り付けるため

機械的強度やピンホールなどによるショートが少ない緻密なセラミックの材料設計が必要となる。

【0008】また、これまで材料を緻密に焼成するために焼成後のグレインサイズを制御しようとして、各種の粒径制御剤が用いられてきた。しかし、これら粒径制御剤も上記の第3の組成物と同様に特性に悪影響を与えることがわかっている。すなわち、Pbを含む圧電材料に用いた場合、Pbと反応してペロブスカイト構造以外の誘電率の低い別の結晶構造を持つ化合物が二次的に形成し、本来の圧電特性が得られなくなってしまうという課題である。

【0009】このように、近年、圧電材料を応用した製品における圧電特性および耐熱性の向上の要望は強く、正方晶系と菱面体晶系の相境界領域の性能を十分引き出さなければならなくなっている。

【0010】本発明は、圧電特性が良好な正方晶系と菱面体晶系の相境界の組成物の材料組成の中でAサイトの鉛の量を制御することにより、良好な圧電特性を有し、かつ耐熱性の高い圧電材料および圧電振動子および圧電発音体を安定に得ることを第1の目的としている。

【0011】また、本発明の第2の目的は、単層で用いられるために高強度で緻密なセラミックが要求される圧電発音体において、圧電材料の性能を十分に引き出しながらグレインサイズの制御が可能となる圧電材料の製造方法を得ることである。

【0012】

【課題を解決するための手段】この課題を解決するための手段として、材料組成中の鉛の量を減少することで本発明は従来にない良好な圧電特性を得ることができた。すなわち、本発明によれば、比誘電率が5000以上で

$(\text{Pb}_{(1-x-\alpha)}\text{M}_\alpha)(\text{Zr}_{(1-y)}\text{Ti}_y)_{(1-z)}(\text{Mg}_{1/3}\text{Nb}_{2/3})_z\text{O}_3$
(Mは、Ba、Bi、Srのうちから選択される少なくとも1種類の元素、 $0 \leq \alpha < 0.10$)

なる化学式で表わされ、かつ $0.005 < x < 0.05$ 、 $0.20 < y < 0.30$ 、 $0.45 < z < 0.55$ の範囲にあるように組成を設定したことを特徴とする圧電材料であり、良好な耐熱性および圧電特性を有し、かつ信頼性の高い圧電材料を得ることができるという作用を有する。

$(\text{Pb}_{(1-\alpha)}\text{M}_\alpha)(\text{Zr}_{(1-y)}\text{Ti}_y)_{(1-z)}(\text{Mg}_{1/3}\text{Nb}_{2/3})_z\text{O}_3$

(Mは、Ba、Bi、Srのうちから選択される少なくとも1種類の元素、 $0 \leq \alpha < 0.10$)

なる化学式で表わされ、かつ $0.20 < y < 0.30$ 、 $0.45 < z < 0.55$ の範囲にあるように材料を仮焼成後、粒径制御剤としてコランバイト型酸化物である MgNb_2O_6 をPbに対して $0.005 < x < 0.05$ の範囲にあるように添加し、再び仮焼成を行う圧電材料の製造方法であり、良好な耐熱性および圧電特性を有し、かつ信頼性の高い圧電材料を得ることができるという作用を有する。

電気機械結合係数が65%以上でキュリー温度が摂氏200度以上の圧電材料およびその適用品を実現することができる。

【0013】また、好ましい粒径制御剤の使用とそれを用いた圧電材料の製造方法により、容易に単層で用いることが可能となる高強度で緻密なセラミックを実現することができる。

【0014】

【発明の実施の形態】請求項1記載の発明は、鉛を含むペロブスカイト型酸化物を主成分とする圧電材料において、

$\text{Pb}_{(1-x)}(\text{Zr}_{(1-y)}\text{Ti}_y)_{(1-z)}(\text{M}_{1/3}\text{Nb}_{2/3})_z\text{O}_3$

(Mは、Mg、Ni、Znのうちから選択される少なくとも1種類の元素)

なる化学式で表わされ、かつ $0.005 < x < 0.05$ 、 $0.50 < y < 0.80$ 、 $0.35 < z < 0.65$ の範囲にあるように組成を設定したことを特徴とする圧電材料であり、良好な耐熱性および圧電特性を有し、かつ信頼性の高い圧電材料を得ることができるという作用を有する。

【0015】請求項2記載の発明は、摂氏200度以上のキュリー点を有することを特徴とする請求項1記載の圧電材料であり、良好な耐熱性および圧電特性を有し、かつ信頼性の高い圧電材料を得ることができるという作用を有する。

【0016】請求項3記載の発明は、鉛を含むペロブスカイト型酸化物を主成分とする圧電材料において、

【数3】

$(\text{Pb}_{(1-x-\alpha)}\text{M}_\alpha)(\text{Zr}_{(1-y)}\text{Ti}_y)_{(1-z)}(\text{Mg}_{1/3}\text{Nb}_{2/3})_z\text{O}_3$
【0017】請求項4記載の発明は、グレインサイズが $5\mu\text{m}$ 以下であることを特徴とする請求項1から3のいずれかに記載の圧電材料であり、良好な耐熱性および圧電特性を有し、かつ信頼性の高い圧電材料を得ることができるという作用を有する。

【0018】請求項5記載の発明は、鉛を含むペロブスカイト型酸化物を主成分とする圧電材料において、

【数4】

う作用を有する。

【0019】請求項6記載の発明は、請求項5記載の圧電材料の製造方法で得られるグレインサイズが $5\mu\text{m}$ 以下である圧電材料であり、良好な耐熱性および圧電特性を有し、かつ信頼性の高い圧電材料を得ることができるという作用を有する。

【0020】請求項7記載の発明は、請求項1から4のいずれか、または請求項6に記載の圧電材料を用いたことを特徴とする圧電振動子であり、良好な耐熱性および

圧電特性を有し、かつ信頼性の高い圧電材料を得ることができるという作用を有する。

【0021】請求項8記載の発明は、厚みが50ミクロン以下の請求項7に記載の圧電材料を用いた圧電振動子であり、良好な耐熱性および圧電特性を有し、かつ信頼性の高い圧電材料を得ることができるという作用を有する。

【0022】請求項9記載の発明は、請求項7または8記載の圧電振動子を用いたことを特徴とする圧電発音体であり、良好な耐熱性および圧電特性を有し、かつ信頼性の高い圧電材料を得ることができるという作用を有する。

【0023】

【実施例】以下、この発明の実施例について図面を参照しながら説明する。図1はこの発明の実施例における正方晶系と菱面体晶系の相境界を有する固相反応で得られる圧電材料の相を示す模式図である。

【0024】この実施例では、チタン酸鉛（化学式 $PbTiO_3$ を以降PTと略す）とジルコン酸鉛（化学式 $PbZrO_3$ を以降PZと略す）とマグネシウムニオブ酸鉛（化学式 $Pb(Mg_{1/3}Nb_{2/3})O_3$ を以降PMNと略す）を固相反応によって所望の組成物を得る場合について説明する。

【0025】いわゆるPZT系は $xPT-(1-x)PZ$ の組成式で表され、 x が0.42から0.48の範囲に正方晶系と菱面体晶系の相境界が存在する。この相境界において、良好な圧電特性をもつ材料であることは一般によく知られている。

【0026】これにPMNを添加した三成分系の圧電材料は、 $xPT-yPZ-(1-x-y)PMN$ の組成式で表される。この材料についても詳細に研究されてお

り、3重点付近で大きな圧電特性をもつが、一方で圧電特性の向上に伴いキュリー点が下がってしまう欠点がある。ここで、正方晶系と菱面体晶系では、菱面体晶系の方が室温近傍における比誘電率の温度変化率が大いことから、一般には正方晶系を用いることが多い。正方晶系においてキュリー点が200℃以上ある材料組成になると、誘電率が高々2000程度であり、圧電特性の大きなものを得ることができない。 $xPT-yPZ-(1-x-y)PMN$ で示される材料で、デバイスから要求される高い圧電特性を得ようとすると、3重点付近に材料組成が限定されてしまうが、このとき材料のキュリー点は150℃以下になってしまう。

【0027】この実施例では、この逐次相転移する強誘電体で使用温度領域で安定な温度特性を示す正方晶系の材料組成において、Aサイトの鉛の量を制御することで良好な圧電特性を有し、かつキュリー点が200度以上の圧電材料を実現した。

【0028】また、 $xPT-yPZ-(1-x-y)PMN$ の組成に粒径制御剤としてニオブ酸マグネシウム（化学式 $MgNb_2O_6$ を以降MNOと略す）を用いることで、Aサイトの鉛量を制御し、粒径制御剤としての効果と良好な圧電特性の両方を同時に実現した。

【0029】この発明の効果は、以下の実施例に記述した材料系に限定されるものではない。また、この発明の効果は、以下の実施例に記述した圧電振動子に限定されるものではない。

【0030】（実施例1）実施例1として以下に示すセラミックスを作製した。作製したPZT系セラミックスの材料組成は、次の（1）から（10）であるが、このうち（2）～（6）は本発明の材料組成によるものである。

- (1) $Pb_{1.00}(Zr_{0.26}Ti_{0.74})_{0.50}(Mg_{1/3}Nb_{2/3})_{0.50}O_3$
- (2) $Pb_{0.99}(Zr_{0.26}Ti_{0.74})_{0.50}(Mg_{1/3}Nb_{2/3})_{0.50}O_3$
- (3) $Pb_{0.98}(Zr_{0.26}Ti_{0.74})_{0.50}(Mg_{1/3}Nb_{2/3})_{0.50}O_3$
- (4) $Pb_{0.97}(Zr_{0.26}Ti_{0.74})_{0.50}(Mg_{1/3}Nb_{2/3})_{0.50}O_3$
- (5) $Pb_{0.96}(Zr_{0.26}Ti_{0.74})_{0.50}(Mg_{1/3}Nb_{2/3})_{0.50}O_3$
- (6) $Pb_{0.95}(Zr_{0.26}Ti_{0.74})_{0.50}(Mg_{1/3}Nb_{2/3})_{0.50}O_3$
- (7) $Pb_{0.94}(Zr_{0.26}Ti_{0.74})_{0.50}(Mg_{1/3}Nb_{2/3})_{0.50}O_3$
- (8) $Pb_{0.93}(Zr_{0.26}Ti_{0.74})_{0.50}(Mg_{1/3}Nb_{2/3})_{0.50}O_3$
- (9) $Pb_{0.92}(Zr_{0.26}Ti_{0.74})_{0.50}(Mg_{1/3}Nb_{2/3})_{0.50}O_3$
- (10) $Pb_{0.91}(Zr_{0.26}Ti_{0.74})_{0.50}(Mg_{1/3}Nb_{2/3})_{0.50}O_3$

【0031】これらで表される組成になるように、 PbO 、 ZrO_2 、 TiO_2 、 MgO 、 Nb_2O_5 の粉末を秤量し、これらの粉末をボールミルで湿式混合してスラリーを作製した。

（工程1）得られたスラリーを脱水して電気炉中で900℃の温度で仮焼成した。

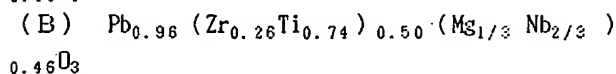
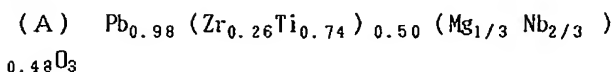
（工程2）得られた仮焼成粉末を1μm以下に粉碎した後、プレス成形によって2ton/cm²の圧力でφ15mm×厚さ3mmの円盤状に成形した。

（工程3）この成形体を1250℃の温度で焼成し、サンプル（1）～（10）を作製した。

こうして得られた最終整形済みの焼結体に電極を付ける。電極材料は、焼き付け銀や導電性塗料や金属を蒸着した。その後に分極処理を行い、電気機械結合係数Kp（%）と誘電率ε、さらにキュリー点について測定した。

【0032】また、上記した作製方法により、下記のサンプル（11）、（12）を作製した。まず、下記の

(A)、(B)を(工程1)および(工程2)で作製する。



その後、(A)、(B)にそれぞれPbに対して(Mg_{1/3}Nb_{2/3})_{0.02}O₃、(Mg_{1/3}Nb_{2/3})_{0.04}O₃となるよ

うにMgNb₂O₆を添加し、上記サンプル(3)、(5)と同じ組成になるようにして、再度仮焼成を行い、仮焼成粉末のサンプル(11)、(12)を作製した。サンプル(11)、(12)に対して上記(工程3)を用いて円盤状の成形を行い、同様にKp、εとキュリー点の測定を行った。この結果を表1に示す。

【0033】

【表1】

サンプル	Kp (%)	ε	キュリー点 (°C)
(1)*	63	3800	210
(2)	70	4500	210
(3)	72	5500	210
(4)	72	5300	210
(5)	73	5300	210
(6)	70	5000	210
(7)*	65	4500	210
(8)*	62	3700	210
(9)*	58	3000	210
(10)*	50	3000	210
(11)	75	6800	210
(12)	75	5750	210

Kpは、圧電セラミックスの電気機械結合係数を示す。

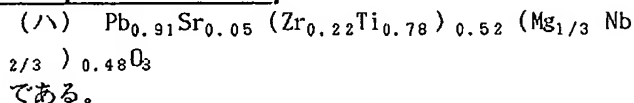
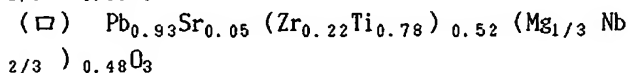
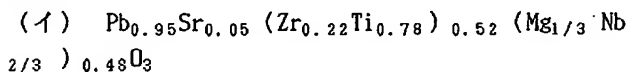
【0034】この結果、電気機械結合係数Kpが70%で比誘電率が5000を超える圧電材料でキュリー点が200℃以上の材料が容易に作製できることがわかる。

【0035】また、Pbに対してMgNb₂O₆を添加し、再度仮焼成を行い、仮焼成粉末を作製することによって、この効果がより顕著に現れる。

【0036】また、サンプル(1)、(5)、(12)のSEM観察写真を見ると、サンプル(5)と(12)はまったく同じ材料組成であるが、サンプル(12)で用いた製造方法により、材料のグレイン制御を効率よく行うことが可能となり、グレインサイズが5μm以下に制御されていることがわかる。

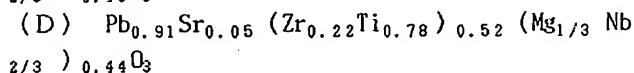
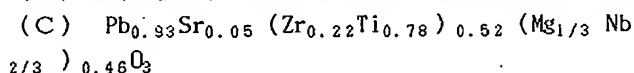
【0037】本発明によるPbを減らす材料組成により、耐熱性と圧電特性の向上を同時に満足することが可能となる。また、本発明で使用する粒径制御剤および圧電材料製造方法によりグレインサイズの制御を行うことが可能であり、デバイスから要求される緻密なセラミックスを容易に実現できる。

【0038】(実施例2)次に、以下に示すセラミックスを作製した。作製したPZT系セラミックスの材料組成は、



【0039】これらで表される組成になるように、実施例1と同様に(工程1)、(工程2)、(工程3)で円盤状の成形体を作製した。この成形体を1250℃の温度で焼成し、サンプル(イ)～(ハ)を作製した。こうして得られた最終整形済みの焼結体に電極を付ける。電極材料は、焼き付け銀や導電性塗料や金属を蒸着した。その後に分極処理を行い、電気機械結合係数Kp(%)と誘電率ε、さらにキュリー点について測定した。

【0040】また、本発明の作製方法により、下記の(ニ)、(ホ)を作製した。まず、下記の(Ｃ)、(Ｄ)を(工程1)および(工程2)で作製する。



【0041】その後、(C)、(D)にそれぞれPbに対して(Mg_{1/3}Nb_{2/3})_{0.02}O₃、(Mg_{1/3}Nb_{2/3})_{0.04}O₃となるようにMgNb₂O₆を添加し、再度仮焼成を行い、仮焼成粉末(ニ)、(ホ)を作製した。(ニ)、(ホ)に対して(工程3)を用いて円盤状の成形を行い、同様にKp、εとキュリー点の測定を行った。

【0042】この結果を表2に示す。

【表2】

サンプル	Kp (%)	ε	キュリー点 (°C)
(イ)	52	2600	205
(ロ)	57	3000	205
(ハ)	56	3100	205
(ニ)	62	3000	205
(ホ)	64	3350	205

Kpは、圧電セラミックスの電気機械結合係数を示す。

【0043】この結果から、Aサイトの鉛の量を制御することで良好な圧電特性を有し、かつキュリー点が200度以上の圧電材料を実現した。また、Pbに対して $MgNb_2O_6$ を添加し、再度仮焼成を行い、仮焼成粉末を作製することによって、この効果がより顕著に現れることがわかる。

【0044】また、本発明で使用する粒径制御剤および圧電材料製造方法によりグレインサイズの制御を行うことが可能であり、デバイスから要求される緻密なセラミックスを容易に実現できる。

【0045】（実施例3）実施例1に示したサンプル（1）～（12）の材料を用いて、焼成後の膜厚が100 μm になるようにグリーンシートを作製し、円盤状に打ち抜いた後、焼成し、銀電極を両面に形成して分極を行った後、振動板を張り付け、バイモルフ型圧電振動子を形成した。その後、可聴域の音圧を測定した。結果を表3に示す。

【0046】

【表3】

サンプル	音圧 (dB)	キュリー点 (°C)
(1)*	100	210
(2)	108	210
(3)	110	210
(4)	110	210
(5)	107	210
(6)	105	210
(7)*	100	210
(8)*	95	210
(9)*	95	210
(10)*	90	210
(11)	115	210
(12)	118	210

サンプル	音圧 (dB)	耐熱試験後	キュリー点 (°C)
(3)	113	112	210
(5)	110	110	210
(11)	120	120	210
(12)	120	121	210

音圧は、周波数1kHzの測定結果。

【0050】表4および表3の比較から、50 μm 以下のセラミック素子を用いることで音圧がより向上することがわかる。また40 μm の薄板の圧電振動子に熱が伝わりやすい場合でも、キュリー点が高いために実用上問題無い耐熱性が得られている。これは、近年デバイス設計から要求される材料の薄板化に対して本発明の材料組成は非常に有効であることを示している。

【0051】また、40 μm の薄板セラミックを作製する場合に、グレインサイズの小さいサンプル（11）、（12）の素子では銀電極のしみ込みがなくなる。この

*印は本発明の範囲外。

音圧は、周波数1kHzの測定結果。

【0047】表3から、本発明の材料組成を用いることでキュリー点の変化なしに高い音圧が得られることがわかる。耐熱性も、実用上問題無かった。さらにサンプル（11）、（12）については、素子の割れや分極時のショートに問題なく高強度なセラミックが実現されている。

【0048】（実施例4）実施例3に示したサンプル（3）、（5）、（11）、（12）の材料を用いて、焼成後の膜厚が40 μm になるようにグリーンシートを作製し、円盤状に打ち抜いた後、焼成し、銀電極を両面に形成して分極を行った後、振動板を張り付け、バイモルフ型圧電振動子を形成した。その後、可聴域の音圧を測定した。また、220°C、60秒の半田付けによる耐熱性試験を行った。結果を表4に示す。

【0049】

【表4】

ため分極時のショート不良が、サンプル（11）、（12）ではまったく問題なかった。すなわち、薄板の素子を作製するには、材料のグレイン制御が必要条件となる。このとき、Pbに対して $MgNb_2O_6$ を添加し、再度仮焼成を行い、仮焼成粉末を作製する方法は非常に有効な手段となる。

【0052】（実施例5）次に実施例5として以下に示す（21）から（25）のセラミックスを作製し、実施例1と同様の実験を行い、圧電特性の測定を行った。また、グリーンシートを作製し、実施例3と同様に、可聴域の音圧を測定した結果を表5に示す。

- (21) $Pb_{1.00}(Zr_{0.40}Ti_{0.60})_{0.60}(Mg_{3/12}Zn_{1/12}Nb_{2/3})_{0.40}O_3$
 (22) $Pb_{0.99}(Zr_{0.40}Ti_{0.60})_{0.60}(Mg_{3/12}Zn_{1/12}Nb_{2/3})_{0.40}O_3$
 (23) $Pb_{0.98}(Zr_{0.40}Ti_{0.60})_{0.60}(Mg_{3/12}Zn_{1/12}Nb_{2/3})_{0.40}O_3$
 (24) $Pb_{0.97}(Zr_{0.40}Ti_{0.60})_{0.60}(Mg_{3/12}Zn_{1/12}Nb_{2/3})_{0.40}O_3$
 (25) $Pb_{0.96}(Zr_{0.40}Ti_{0.60})_{0.60}(Mg_{3/12}Zn_{1/12}Nb_{2/3})_{0.40}O_3$

【0053】

【表5】

サンプル	K _p (%)	ε	音圧 (dB)	キュリー点 (°C)
(21)*	*60	3900	99	220
(22)	65	4900	103	220
(23)	72	5000	107	220
(24)	70	5200	107	220
(25)	68	5000	105	220

*印は本発明の範囲外。K_pは、圧電セラミックスの電気機械結合係数を示す。音圧は、周波数1kHzの測定結果。

【0054】この結果から、 $Pb_{(1-x)}(Zr_{(1-y)}Ti_y)_{(1-z)}(Ni_{3/12}Zn_{1/12}Nb_{2/3})_zO_3$ の場合においても本発明の効果が得られることがわかる。

【0055】

【発明の効果】この発明によれば、キュリー温度が摂氏200度以上でかつ圧電特性および信頼性の高い圧電材料が容易に実現可能となる。また、本製造方法を用いることで、この効果がより顕著になるだけでなく、セラミック素子を作製する場合のグレインサイズの制御が同時に可能となる。

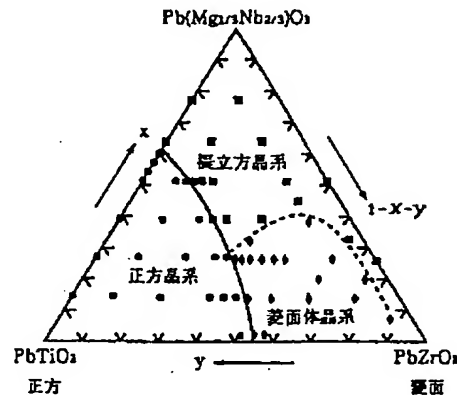
【0056】この発明の効果は、実施例に記述した圧電振動子に限定されず、アクチュエータや加速度センサーなど、圧電磁器を用いた様々なデバイスに適用できることはいふまでもない。

【0057】この材料の実現によりデバイス設計から要望されていた耐熱性と高圧電特性、高信頼性の両立が可能となる。またこの製造方法により、同じくデバイス側から要求される薄板圧電素子の分極時のショート不良の抑制が可能となり、生産性の向上を図ることが可能となる。

【図面の簡単な説明】

【図1】 $xPT-yPZ-(1-x-y)PMN$ の圧電材料の相を示す模式図

【図1】



フロントページの続き

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KUWATA JUN
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(30)Priority

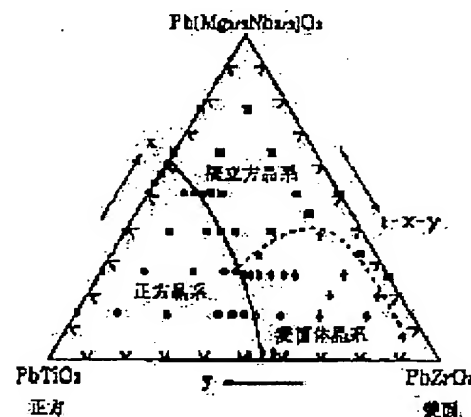
Priority number : 09121228 Priority date : 12.05.1997 Priority country : JP

(54) PIEZOELECTRIC MATERIAL AND ITS PRODUCTION AND PIEZOELECTRIC
OSCILLATOR AND PIEZOELECTRIC SOUNDING BODY USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To stably obtain a piezoelectric material comprising a material composition having a composition of phase boundary between a good tetragonal system and a good rhombohedral system, in an oxide ferroelectric ceramic used for various kinds of electronic parts, and to use a particle diameter-controlling agent capable of sufficiently pulling out the performances of the piezoelectric material and simultaneously controlling the sizes of grains, in a piezoelectric sounding body requiring a highly strong and compact ceramic.

SOLUTION: This piezoelectric material containing as a main component a perovskite type oxide containing iron is produced by calcining a material of the formula $(\text{Pb}(1-x-\alpha)\text{M}\alpha)(\text{Zr}(1-y)\text{Ti}y)(1-z)$



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(Mg_{2/3})zO₃ [M is at least one element selected from Ba, Bi and Sr; $0 \leq (\alpha) < 0.10$; $0.20 < (y) < 0.30$; $0.45 < (z) < 0.55$, adding MgNb₂O₆ of columbite type oxide as a grain diameter-controlling agent in an amount range: $0.005 < (x) < 0.05$ based on Pb and again calcining the mixture.

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JAPANESE

[JP,11-029357,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS
DRAWINGS

[Translation done.]

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CLAIMS

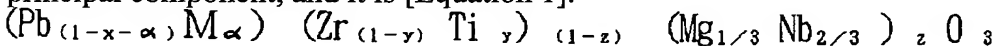
[Claim(s)]

[Claim 1] The perovskite mold oxide containing lead is set to the piezoelectric material used as a principal component, and it is $\text{Pb}(1-x) \text{Zr}_x \text{O} (\text{M}_{1/3} \text{Nb}_{2/3})_3$ (at least one kind of element with which M is chosen from among Mg, nickel, and Zn) $(1(\text{Zr}(1-y) \text{Ti}_y)-z)$.

Piezoelectric material characterized by setting up a presentation as it is expressed with the becoming chemical formula and is in the range of $0.005 < x < 0.055$, $0.50 < y < 0.80$, and $0.35 < z < 0.65$.

[Claim 2] Piezoelectric material according to claim 1 characterized by having the Curie point of 200-degree more than Centigrade.

[Claim 3] The perovskite mold oxide containing lead is set to the piezoelectric material used as a principal component, and it is [Equation 1].

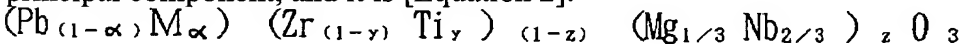


(At least one kind of element, $0 \leq \alpha < 0.10$ as which M is chosen from among Ba, Bi, and Sr)

Piezoelectric material characterized by setting up a presentation as it is expressed with the becoming chemical formula and is in the range of $0.005 < x < 0.05$, $0.20 < y < 0.30$, and $0.45 < z < 0.55$.

[Claim 4] Piezoelectric material given in either of claims 1-3 characterized by grain size being 5 micrometers or less.

[Claim 5] The perovskite mold oxide containing lead is set to the piezoelectric material used as a principal component, and it is [Equation 2].



(At least one kind of element, $0 \leq \alpha < 0.10$ as which M is chosen from among Ba, Bi, and Sr)

MgNb_2O_6 which is a choline cutting tool mold oxide considering an ingredient after temporary baking and as a particle-size control material as it is expressed with the becoming chemical formula and is in the range of $0.20 < y < 0.30$ and $0.45 < z < 0.55$. The manufacture approach of piezoelectric material of adding as it is in the range of $0.005 < x < 0.05$ to Pb, and performing temporary baking again.

[Claim 6] Piezoelectric material whose grain size obtained by the manufacture approach of a piezoelectric material according to claim 5 is 5 micrometers or less.

[Claim 7] The piezoelectric transducer characterized by using either of claims 1-4, or a piezoelectric material according to claim 6.

[Claim 8] The piezoelectric transducer [thickness] using a piezoelectric material 50 microns or less according to claim 7.

[Claim 9] The piezo-electric sounding body characterized by using a piezoelectric transducer according to claim 7 or 8.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the piezoelectric material used for sources of pronunciation, such as a portable telephone and a computer, its manufacture approach, the piezoelectric transducer using it, and the piezo-electric sounding body.

[0002]

[Description of the Prior Art] In recent years, it has had a better opinion of the piezoelectric loudspeaker and receiver using piezoelectric material as an audio output device of a cellular phone or a computer. The request to the piezoelectric transducer which operates to stability at the elevated temperature of 200-degree more than Centigrade especially as portable is strong. At this time, 1 thermal resistance, 2 piezo-electricity property, and 3 dependability pose a problem. Therefore, much retrieval of the exotic material which perceived the ceramics of an oxide ferroelectric which has a perovskite structure, and improvements by the additive are made.

[0003] If it is going to improve a piezo-electric property in the ceramics of an oxide ferroelectric, the Curie point (transition temperature of a ferroelectric phase and a paraelectric phase) will fall, and thermal resistance will worsen. Attention needed to be paid to thermal resistance, when Yuzu made the Curie point less than 200 degrees for thermal resistance to some extent and an ingredient was used, in order to acquire the good property demanded. Consequently, there was a problem that a property will change, in the electrical connection process of the ejection electrode from an ingredient.

[0004] Moreover, in the presentation to which the Curie point currently demanded from the device design becomes 200-degree more than Centigrade, the piezo-electric big property was no longer acquired, and there was a problem of it becoming impossible to meet the request to a piezo-electric property.

[0005]

[Problem(s) to be Solved by the Invention] Then, although the compound perovskite mold oxide used as the 3rd constituent is further mixed as ingredient retrieval for acquiring the good property for which it asks or newly adding [many] an additive have been studied By mixing the 3rd constituent, the compound with another crystal structure with low dielectric constants other than a perovskite structure was formed secondarily, and the new technical problem that an original piezo-electric property was no longer acquired occurred.

[0006] Moreover, a miniaturization and thin shape-ization are requested more from the device, therefore the requests of the ceramics of a thin film have been mounting. Although the request of the sounding body 2mm or less has come out as the piezo-electric sounding body, if it is going to respond to this, the ceramic of sheet metal 50 microns or less is needed as a design top ceramic component of the sounding body.

[0007] Furthermore, in order to stick on a metal plate the ceramic used for the piezo-electric sounding body by the monolayer unlike a laminating type like a stacked type ceramic condenser or an actuator, the materials design of a precise ceramic with little short-circuit by the mechanical strength, a pinhole, etc. is needed.

[0008] Moreover, it was going to control the grain size after calcinating in order to calcinate an ingredient precisely, and various kinds of particle-size control agents have so far been used.

However, it turns out that it has a bad influence on a property like [these particle-size control agent] the 3rd above-mentioned constituent. That is, when it uses for the piezoelectric material containing Pb, the compound which reacts with Pb and has another crystal structure with low dielectric constants other than a perovskite structure is the technical problem that form secondarily and an original piezo-electric property is no longer acquired.

[0009] The request of improvement in the piezo-electric property in the product adapting piezoelectric material and thermal resistance is strong, and must be stopping thus, having to pull out enough the engine performance of the phase border area of tetragonal system and a rhombohedral system in recent years.

[0010] This invention sets it as the 1st purpose to have a good piezo-electric property and to obtain a high piezoelectric material, a heat-resistant piezoelectric transducer, and the heat-resistant piezo-electric sounding body to stability, when a piezo-electric property controls the amount of the lead of A site in the ingredient presentation of the constituent of the phase boundary of good tetragonal system and a rhombohedral system.

[0011] Moreover, the 2nd purpose of this invention is acquiring the manufacture approach of the piezoelectric material which becomes controllable [grain size], fully pulling out the engine performance of piezoelectric material in the piezo-electric sounding body as which a precise ceramic is required with high intensity, since it is used by the monolayer.

[0012]

[Means for Solving the Problem] As this The means for solving a technical problem, this invention was able to acquire the good piezo-electric property which is not in the former by decreasing the amount of the lead under ingredient presentation. That is, according to this invention, Curie temperature can realize [specific inductive capacity / an electromechanical coupling coefficient] the piezoelectric material and its application article of 200-degree more than Centigrade at 65% or more or more by 5000.

[0013] Moreover, a precise ceramic is realizable with the high intensity which becomes possible [using by the monolayer easily] by the manufacture approach of the piezoelectric material using use and it of a desirable particle-size control agent.

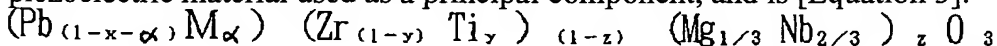
[0014]

[Embodiment of the Invention] Invention according to claim 1 sets the perovskite mold oxide containing lead to the piezoelectric material used as a principal component, and is $\text{Pb}_{(1-x)}\text{Zr}_x\text{O}_{(1-y)}\text{Ti}_y\text{O}_z$ (at least one kind of element with which M is chosen from among Mg, nickel, and Zn) $(\text{Zr}_{(1-y)}\text{Ti}_y)_{(1-z)}$.

As it is expressed with the becoming chemical formula and is in the range of $0.005 < x < 0.055$, $0.50 < y < 0.80$, and $0.35 < z < 0.65$, it is the piezoelectric material characterized by setting up a presentation, and it has good thermal resistance and a piezo-electric property, and has an operation that a reliable piezoelectric material can be obtained.

[0015] Invention according to claim 2 is a piezoelectric material according to claim 1 characterized by having the Curie point of 200-degree more than Centigrade, and it has good thermal resistance and a piezo-electric property, and it has an operation that a reliable piezoelectric material can be obtained.

[0016] Invention according to claim 3 sets the perovskite mold oxide containing lead to the piezoelectric material used as a principal component, and is [Equation 3].

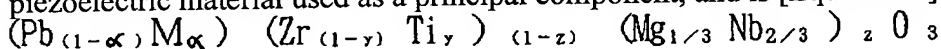


(At least one kind of element, $0 \leq \alpha < 0.10$ as which M is chosen from among Ba, Bi, and Sr)

As it is expressed with the becoming chemical formula and is in the range of $0.005 < x < 0.05$, $0.20 < y < 0.30$, and $0.45 < z < 0.55$, it is the piezoelectric material characterized by setting up a presentation, and it has good thermal resistance and a piezo-electric property, and has an operation that a reliable piezoelectric material can be obtained.

[0017] Invention according to claim 4 is a piezoelectric material given in either of claims 1-3 characterized by grain size being 5 micrometers or less, and it has good thermal resistance and a piezo-electric property, and it has an operation that a reliable piezoelectric material can be obtained.

[0018] Invention according to claim 5 sets the perovskite mold oxide containing lead to the piezoelectric material used as a principal component, and is [Equation 4].



(At least one kind of element, $0 \leq \alpha < 0.10$ as which M is chosen from among Ba, Bi, and Sr)

As it is expressed with the becoming chemical formula and is in the range of $0.20 < y < 0.30$ and $0.45 < z < 0.55$, an ingredient After temporary baking, MgNb 2O6 which is a cholane cutting tool mold as a particle-size control agent It adds, as it is in the range of $0.005 < x < 0.05$ to Pb. It is the manufacture approach of piezoelectric material of performing temporary baking again, and it has good thermal resistance and a piezo-electric property, and has an operation that a reliable piezoelectric material can be obtained.

[0019] The grain size obtained by the manufacture approach of a piezoelectric material according to claim 5 is the piezoelectric material which is 5 micrometers or less, it has good thermal resistance and a piezo-electric property, and invention according to claim 6 has an operation that a reliable piezoelectric material can be obtained.

[0020] Invention according to claim 7 is a piezoelectric transducer characterized by using either of claims 1-4, or a piezoelectric material according to claim 6, and it has good thermal resistance and a piezo-electric property, and it has an operation that a reliable piezoelectric material can be obtained.

[0021] Thickness is the piezoelectric transducer which used a piezoelectric material 50 microns or less according to claim 7, it has good thermal resistance and a piezo-electric property, and invention according to claim 8 has an operation that a reliable piezoelectric material can be obtained.

[0022] Invention according to claim 9 is the piezo-electric sounding body characterized by using a piezoelectric transducer according to claim 7 or 8, and it has good thermal resistance and a piezo-electric property, and it has an operation that a reliable piezoelectric material can be obtained.

[0023]

[Example] Hereafter, it explains, referring to a drawing about the example of this invention. Drawing 1 is the mimetic diagram showing the phase of the piezoelectric material obtained by the solid phase reaction which has the phase boundary of tetragonal system and a rhombohedral system in one example of this invention.

[0024] This example explains the case where the constituent of a request of lead titanate (a chemical formula PbTiO_3 is henceforth abbreviated to PT), lead zirconate (a chemical formula PbZrO_3 is henceforth abbreviated to PZ), and magnesium niobic acid lead (chemical formula $\text{Pb}(\text{Mg}_{1/3} \text{Nb}_{2/3})\text{O}_3$ is henceforth abbreviated to PMN) by solid phase reaction is obtained.

[0025] The so-called PZT system is expressed with the empirical formula of $x\text{PT}-(1-x)\text{PZ}$, and the phase boundary of tetragonal system and a rhombohedral system exists [x] in the range of 0.42 to 0.48. Generally on this phase boundary, it is known well that it is an ingredient with a good piezo-electric property.

[0026] The piezoelectric material of the three-component system which added PMN to this is expressed with the empirical formula of $x\text{PT}-y\text{PZ}-(1-x-y)\text{PMN}$. Although the detail inquires also about this ingredient and it has a piezo-electric big property near 3 importance, there is a fault in which the Curie point falls with improvement in a piezo-electric property in one side. Here, generally in tetragonal system and a rhombohedral system, tetragonal system is used in many cases from the rate of a temperature change of specific inductive capacity [direction / of a rhombohedral system / near the room temperature] being large. If 200 degrees C or more of Curie points become a certain ingredient presentation in tetragonal system, a dielectric constant is at most about 2000, and what has a piezo-electric big property cannot be obtained. Although an ingredient presentation will be limited near 3 importance if it is going to acquire the piezo-electric high property demanded from a device with the ingredient shown by $x\text{PT}-y\text{PZ}-(1-x-y)\text{PMN}$, the Curie point of an ingredient will become 150 degrees C or less at this time.

[0027] It has a good piezo-electric property by controlling the amount of the lead of A site by this example in the ingredient presentation of the tetragonal system which shows the stable temperature characteristic in a service temperature field with this ferroelectric that carries out phase transition serially, and the Curie point realized piezoelectric material of 200 degrees or more.

[0028] Moreover, the lead of A site was controlled by using niobic acid magnesium (a chemical formula MgNb_2O_6 being henceforth abbreviated to MNO) for the presentation of $x\text{PT}-y\text{PZ}-(1-x-y)$ PMN as a particle-size control agent, and both the effectiveness as a particle-size control agent and a good piezo-electric property were realized to coincidence by it.

[0029] This effect of the invention is not limited to the ingredient system described in the following examples. Moreover, this effect of the invention is not limited to the piezoelectric transducer described in the following examples.

[0030] (Example 1) The ceramics shown below as an example 1 was produced. Although the ingredient presentation of the produced PZT system ceramics is (1) to the following (10), (2) - (6) is based on the ingredient presentation of this invention.

(1) $\text{Pb}_{1.00}(\text{Zr}_{0.26}\text{Ti}_{0.74})_{0.50}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.50}\text{O}_3$ (2) $\text{Pb}_{0.99}(\text{Zr}_{0.26}\text{Ti}_{0.74})_{0.50}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.50}\text{O}_3$ (3) $\text{Pb}_{0.98}(\text{Zr}_{0.26}\text{Ti}_{0.74})_{0.50}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.50}\text{O}_3$ (4) $\text{Pb}_{0.97}(\text{Zr}_{0.26}\text{Ti}_{0.74})_{0.50}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.50}\text{O}_3$ (5) $\text{Pb}_{0.96}(\text{Zr}_{0.26}\text{Ti}_{0.74})_{0.50}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.50}\text{O}_3$ (6) $\text{Pb}_{0.95}(\text{Zr}_{0.26}\text{Ti}_{0.74})_{0.50}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.50}\text{O}_3$ (7) $\text{Pb}_{0.94}(\text{Zr}_{0.26}\text{Ti}_{0.74})_{0.50}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.50}\text{O}_3$ (8) $\text{Pb}_{0.93}(\text{Zr}_{0.26}\text{Ti}_{0.74})_{0.50}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.50}\text{O}_3$ (9) $\text{Pb}_{0.92}(\text{Zr}_{0.26}\text{Ti}_{0.74})_{0.50}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.50}\text{O}_3$ (10) $\text{Pb}_{0.91}(\text{Zr}_{0.26}\text{Ti}_{0.74})_{0.50}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.50}\text{O}_3$ [0031] They are PbO , ZrO_2 , TiO_2 , MgO , and Nb_2O_5 so that it may become the presentation expressed with these. Weighing capacity of the powder was carried out, wet blending of these powder was carried out with the ball mill, and the slurry was produced.

(Process 1) The obtained slurry was dehydrated and temporary baking was carried out at the temperature of 900 degrees C in the electric furnace.

(Process 2) They are 2 ton/cm² by press forming after grinding the obtained temporary baking powder to 1 micrometer or less. It fabricated by the pressure to discoid with a $\phi 15\text{mm} \times$ thickness of 3mm.

(Process 3) This Plastic solid was calcinated at the temperature of 1250 degrees C, and sample (1) - (10) was produced.

In this way, an electrode is attached to the obtained sintered compact [finishing / the last plastic surgery]. The electrode material could be burned and vapor-deposited silver and a conductive paint metallurgy group. Polarization processing was performed after that and it measured about the Curie point to the electromechanical coupling coefficient K_p (%), the dielectric constant epsilon, and the $\tan \delta$.

[0032] Moreover, the following sample (11) and (12) were produced by the above-mentioned production approach. first, the following (A) and (B) -- and (process 1) (process 2) it produces.

(A) $\text{Pb}_{0.98}(\text{Zr}_{0.26}\text{Ti}_{0.74})_{0.50}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.48}\text{O}_3$ (B) After that [$\text{Pb}_{0.96}(\text{Zr}_{0.26}\text{Ti}_{0.74})_{0.50}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.46}\text{O}_3$], (A), It is MgNb_2O_6 so that it may be set to 0.02 ($\text{Mg}_{1/3}\text{Nb}_{2/3}$) O_3 and 0.04 ($\text{Mg}_{1/3}\text{Nb}_{2/3}$) O_3 to Pb at (B), respectively. It adds. As it became the same presentation as the above-mentioned sample (3) and (5), temporary baking was performed again, and the sample (11) of temporary baking powder and (12) were produced. Disc-like shaping was performed using the above (process 3) to a sample (11) and (12), and measurement of K_p , epsilon, and the Curie point was performed similarly. This result is shown in Table 1.

[0033]

Table 1

サンプル	K_p (%)	ϵ	キュリー点 (°C)
(1) *	63	3800	210
(2)	70	4500	210
(3)	72	5500	210
(4)	72	5300	210
(5)	73	5300	210
(6)	70	5000	210
(7) *	65	4500	210
(8) *	62	3700	210
(9) *	58	3000	210
(10) *	50	3000	210
(11)	75	5800	210
(12)	75	5750	210

K_p shows the electromechanical coupling coefficient of electrostrictive ceramics.

[0034] Consequently, it turns out that an ingredient 200 degrees C or more can produce [the Curie point] easily with the piezoelectric material with which specific inductive capacity exceeds [an electromechanical coupling coefficient k_p] 5000 at 70%.

[0035] Moreover, it is MgNb_2O_6 to Pb. This effectiveness shows up more notably by adding, performing temporary baking again and producing temporary baking powder.

[0036] Moreover, although a sample (5) and (12) are the completely same ingredient presentations when the SEM observation photograph of a sample (1), (5), and (12) is seen, it turns out that the manufacture approach used with the sample (12) enables it to perform grain control of an ingredient efficiently, and grain size is controlled by 5 micrometers or less.

[0037] The ingredient presentation which reduces Pb by this invention enables it to be satisfied with coincidence of improvement in thermal resistance and a piezo-electric property. Moreover, it is possible to control grain size by the particle-size control agent and the piezoelectric-material manufacture approach of using it by this invention, and the precise ceramic demanded from a device can be realized easily.

[0038] (Example 2) Next, the ceramics shown below was produced. The ingredient presentation of the produced PZT system ceramics (**) $\text{Pb}_{0.95}\text{Sr}_{0.05}(\text{Zr}_{0.22}\text{Ti}_{0.78})_{0.52}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.48}\text{O}_3$ (**) $\text{Pb}_{0.93}\text{Sr}_{0.05}(\text{Zr}_{0.22}\text{Ti}_{0.78})_{0.52}()$ [$\text{Mg}_{1/3}\text{Nb}_{2/3}$] 0.48O_3 (Ha) It is $\text{Pb}_{0.91}\text{Sr}_{0.05}(\text{Zr}_{0.22}\text{Ti}_{0.78})_{0.52}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.48}\text{O}_3$.

[0039] The disc-like Plastic solid was produced at (the process 2) and the (process 3) as well as (process 1) an example 1 so that it might become the presentation expressed with these. this Plastic solid -- the temperature of 1250 degrees C -- calcinating -- sample (**) - (Ha) was produced. In this way, an electrode is attached to the obtained sintered compact [finishing / the last plastic surgery]. The electrode material could be burned and vapor-deposited silver and a conductive paint metallurgy group. Polarization processing was performed after that and it measured about the Curie point to the electromechanical coupling coefficient K_p (%), the dielectric constant epsilon, and the pan.

[0040] Moreover, following (d) and (e) were produced by the production approach of this invention. first, the following (C) and (D) -- and (process 1) (process 2) it produces.

(C) $\text{Pb}_{0.93}\text{Sr}_{0.05}(\text{Zr}_{0.22}\text{Ti}_{0.78})_{0.52}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.46}\text{O}_3$ (D) $\text{Pb}_{0.91}\text{Sr}_{0.05}(\text{Zr}_{0.22}\text{Ti}_{0.78})_{0.52}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.44}\text{O}_3$ [0041] Then, it is MgNb_2O_6 so that it may be set to $0.02(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and $0.04(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ to Pb at (C) and (D), respectively. It added, temporary baking was performed again and temporary baking powder (d) and (e) were produced. (**) and (**) -- receiving (process 3) -- it used, disc-like shaping was performed and measurement of K_p , epsilon, and the Curie point was performed similarly.

[0042] This result is shown in Table 2.

[Table 2]

サンプル	K_p (%)	ϵ	キュリー点 (°C)
(イ)	52	2600	205
(ロ)	57	3000	205
(ハ)	56	3100	205
(ニ)	62	3000	205
(ホ)	64	3360	205

K_p shows the electromechanical coupling coefficient of electrostrictive ceramics.

[0043] From this result, it has a good piezo-electric property by controlling the amount of the lead of A site, and the Curie point realized piezoelectric material of 200 degrees or more. Moreover, it is MgNb_2O_6 to Pb. By adding, performing temporary baking again and producing temporary baking powder shows that this effectiveness shows up more notably.

[0044] Moreover, it is possible to control grain size by the particle-size control agent and the piezoelectric-material manufacture approach of using it by this invention, and the precise ceramic demanded from a device can be realized easily.

[0045] (Example 3) After having calcinated, having formed the silver electrode in both sides, after having produced the green sheet using the ingredient of sample (1) - (12) shown in the example 1 so that the thickness after baking might be set to 100 micrometers, and piercing disc-like, and performing polarization, the diaphragm was stuck and the bimorph mold piezoelectric transducer

was formed. Then, the sound pressure of a audio range was measured. A result is shown in Table 3.

[0046]

[Table 3]

サンプル	音圧 (dB)	キュリー点 (°C)
(1) *	100	210
(2)	108	210
(3)	110	210
(4)	110	210
(5)	107	210
(6)	105	210
(7) *	100	210
(8) *	95	210
(9) *	95	210
(10) *	90	210
(11)	115	210
(12)	118	210

* This invention of mark is out of range.

Sound pressure is with a frequency of 1kHz as a result of measurement.

[0047] Table 3 shows that sound pressure high without change of the Curie point is obtained by using the ingredient presentation of this invention. Thermal resistance did not have a problem practically, either. Furthermore about a sample (11) and (12), the satisfactory and high intensity ceramic is realized short at the time of the crack of a component, or polarization.

[0048] (Example 4) After having calcinated, having formed the silver electrode in both sides, after having produced the green sheet using the ingredient of the sample (3) shown in the example 3, (5), (11), and (12) so that the thickness after baking might be set to 40 micrometers, and piercing disc-like, and performing polarization, the diaphragm was stuck and the bimorph mold piezoelectric transducer was formed. Then, the sound pressure of a audio range was measured. Moreover, the heat resistance test by 220 degrees C and soldering for 60 seconds was performed. A result is shown in Table 4.

[0049]

[Table 4]

サンプル	音圧 (dB)	耐熱試験後	キュリー点 (°C)
(3)	113	112	210
(5)	110	110	210
(11)	120	120	210
(12)	120	121	210

Sound pressure is with a frequency of 1kHz as a result of measurement.

[0050] The comparison of Table 4 and 3 shows that sound pressure improves more by using a ceramic component 50 micrometers or less. Moreover, the thermal resistance which does not have heat in the piezoelectric transducer of 40-micrometer sheet metal a problem practically at a propagation or cone case since the Curie point is high is obtained. It is shown to sheet-metal-izing of the ingredient with which this is demanded from a device design in recent years that the ingredient presentation of this invention is very effective.

[0051] Moreover, when producing a 40-micrometer sheet metal ceramic, the penetration of a silver electrode is lost with the component of a sample with small grain size (11), and (12). For this reason, short [at the time of polarization / poor] was satisfactory at all at a sample (11) and (12). That is, in order to produce the component of sheet metal, grain control of an ingredient serves as a requirement. It is [as opposed to / at this time / Pb] MgNb₂O₆. It adds, temporary baking is performed again and the approach of producing temporary baking powder serves as a very effective means.

[0052] (Example 5) The ceramics of (21) to (25) shown below as an example 5 was produced, the same experiment as an example 1 was conducted, and the piezo-electric property was measured. Moreover, a green sheet is produced and the result of having measured the sound pressure of a audio range is shown in Table 5 like an example 3.

(21)Pb_{1.00}(Zr_{0.40}Ti_{0.60})_{0.60}(Mg_{3/12}Zn_{1/12}Nb_{2/3})_{0.40}O₃ (22)Pb_{0.99}(Zr_{0.40}Ti_{0.60})_{0.60}

(Mg₃/12Zn₁/12Nb₂/3)0.40O₃ (23)Pb_{0.98}(Zr_{0.40}Ti_{0.60})0.60(Mg₃/12Zn₁/12Nb₂/3)0.40O₃ (24)
Pb_{0.97}(Zr_{0.40}Ti_{0.60})0.60(Mg₃/12Zn₁/12Nb₂/3)0.40O₃ (25)Pb_{0.96}(Zr_{0.40}Ti_{0.60})0.60
(Mg₃/12Zn₁/12Nb₂/3)0.40O₃ [0053]
[Table 5]

サンプル	K _p (%)	ε	音圧 (dB)	キュリー点 (°C)
(21)*	*60	3900	99	220
(22)	65	4900	103	220
(23)	72	5000	107	220
(24)	70	5200	107	220
(25)	68	5000	105	220

* This invention of mark is out of range. K_p shows the electromechanical coupling coefficient of electrostrictive ceramics. Sound pressure is with a frequency of 1kHz as a result of measurement.

[0054] This result to Pb(1-x) z O₃ (1(Zr(1-y) Ti_y)-z) (nickel₃/12Zn₁/12Nb₂/3) It turns out that the effectiveness of this invention is acquired at a case.

[0055]

[Effect of the Invention] According to this invention, Curie temperature is 200-degree more than Centigrade, and piezoelectric material with high piezo-electric property and dependability becomes realizable easily. Moreover, this effectiveness not only becomes more remarkable, but control of the grain size in the case of producing a ceramic component becomes possible by using this manufacture approach at coincidence.

[0056] It cannot be overemphasized that this effect of the invention is not limited to the piezoelectric transducer described in the example, but it can apply to various devices using piezoelectric ceramics, such as an actuator and an acceleration sensor.

[0057] It becomes compatible [the thermal resistance currently demanded from the device design by implementation of this ingredient, a high piezo-electricity property, and high-reliability]. Moreover, by this manufacture approach, control short [at the time of polarization of a sheet metal piezoelectric device similarly demanded from a device side / poor] is attained, and it becomes possible to aim at improvement in productivity.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The mimetic diagram showing the phase of the piezoelectric material of xPT-yPZ-(1-x-y) PMN

[Translation done.]

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